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# ALLYL REARRANGEMENTS: REPORT IX, ACTIVITY OF SODIUM SALTS OF DIALKYLPHOSPHORIC ACIDS AND ESTERS OF PHOSPHORIC ACIDS ON ISOMERIC METHOXYCHLOROPENTENES

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[A Digest]

The activity of the sodium salts of diethylphosphoric, dimethylphosphoric, diisobutylphosphoric acids, trimethylphosphite, and triethylphosphite on isomeric methoxychloropentenes as well as isomeric methoxychloropentenes on the methyl and ethyl ethers of phosphoric acid is described.

The following studies were conducted:

1. Activity of 1-methoxy-5-chloropentene-3 on sodium diethylphosphate
2. 1-methoxy-5-diethylphosphonepentene-3
   a. Activity with water
   b. Saponification with HCl
   c. Titration with bromine
   d. Oxidation with perphthalic acid
   e. Oxidation with potassium permanganate
3. Activity of 1-methoxy-5-chloropentene-3 on sodium dissobutylphosphate
4. Activity of 1-methoxy-5-chloropentene-3 on sodium dimethylphosphate (three experiments)



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5. Reaction between 1-methoxy-3-chloropentene-4 and sodium diethylphosphate in the presence of diethylphophoric acid

6. Activity of 1-methoxy-5-chloropentene-3 on sodium diethylphosphate in the presence of diethylphosphoric acid

7. Activity of 1-methoxy-3-chloropentene-4 on sodium diisobutylphosphate in the presence of diisobutylphosphoric acid

8. Activity of 1-methoxy-3-chloropentene-4 on sodium diethylphosphate

9. Activity of 1-methoxy-3-chloropentene-4 on potassium diethylphosphate

10. Fraction with boiling point 216-217 degrees at 11 millimeters of mercury

    a. Activity with water

    b. Activity with methyl iodide

    c. Activity with copper chloride

    d. Activity with bromine and perphthalic acid

    e. Saponification with HCl

11. Activity of 1-methoxy-3-chloropentene-4 on sodium diisobutylphosphate

12. Activity of 1-methoxy-3-chloropentene-4 on sodium dimethylphosphate

13. Activity of diethylphosphoric acid on 1-methoxy-5-diethylphosphonepentene-3

14. Reaction between 1-methoxy-5-diethylphosphonepentene-3, sodium diethylphosphate, and 1-methoxy-3-chloropentene-4 (2 experiments)

15. Reaction between sodium diethylphosphate and 1-methoxy-3-chloropentene-4

16. Reaction between 1-methoxy-5-diethylphosphonepentene-3, sodium diethylphosphate, and 1-methoxy-5-chloropentene-3

17. Reaction between 1-methoxy-5-diisobutylphosphonepentene-3, sodium diisobutylphosphate, and 1-methoxy-3-chloropentene-4

18. Activity of sodium diethylphosphate on 1-methoxy-5-diethylphosphonepentene-3

19. Reaction between trimethylphosphite and 1-methoxy-5-chloropentene-3

20. Reaction between trimethylphosphite and 1-methoxy-3-chloropentene-4

21. Reaction between triethylphosphite and 1-methoxy-5-chloropentene-3

22. Reaction between triethylphosphite and 1-methoxy-3-chloropentene-4

This study of the activity of 1-methoxy-5-chloropentene-3 on the sodium salts of dimethylphosphoric, diethylphosphoric, and diisobutylphosphoric acids shows that the reactions proceed normally, without the occurrence of allyl rearrangements, and with the formation of corresponding 1-methoxy-5-dialkylphosphone-3-pentenes.

The course of the reactions between 1-methoxy-3-chloropentene-4 and the sodium salts of diethylphosphoric and diisobutylphosphoric acids depends essentially on the presence or absence of free dialkylphosphoric acids. In the first case, the reaction proceeds with allyl rearrangement and the formation of corresponding 1-methoxy-5-dialkylphosphone-3-pentenes, and in the second case, with the formation of fractions with boiling points of 216-217 degrees at 11 millimeters of mercury and



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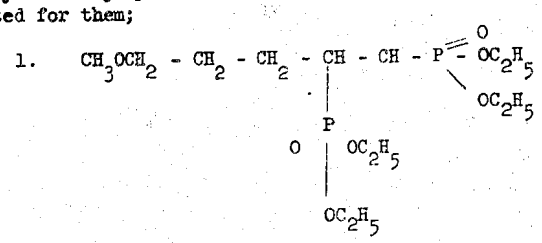
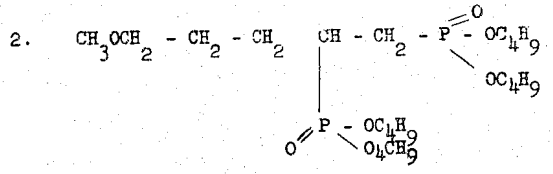
237 degrees at 10 millimeters of mercury, respectively. On the basis of the study of the properties of these two products, the following formulae are suggested for them;

1. 

2. 

The mechanism of the formation of these two products is suggested and confirmed.

It is also shown that the reactions between 1-methoxy-5-chloropentene-3 and the complete esters (polnyye efiry) of phosphoric acid proceed normally, without allyl rearrangement, and lead to the formation of the corresponding 1-methoxy-5-dialkylphosphone-3-pentenes.

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